# **PCT**

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



A61F 13/15, A61M 1/00	A1	0			
<u></u> &			3) International Publication Date: , 12 August 1999 (12.08.99		
21) International Application Number: PC 22) International Filing Date: 4 February 1	CT/US99/02 1999 (04.02.	(81) Designated States: AU, BR, CA, CN, NZ, European pater (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT LU, MC, NL, PT, SE).			
30) Priority Data: 09/018,521 4 February 1998 (04.0	02.98)	ÚŠ	Published  With international search report.		
71) Applicant: CAPITOL VIAL, INC. [US/US]; Drive, Fultonville, NY_12072 (US).	151 Rivers	side			
72) Inventor: HEKAL, Ihab, M.; 121 Blackberry D CT 06903 (ÜS). "	rive, Stamfo	ord,	April Me		
74) Agent: SCHINDLER, Barry, J., Dreier & Ba floor, 499 Park Avenue, New York, NY 100	aritz LLP, 2 022 (US).	Oth			
abace parts and a second parts are second parts and a second parts are second parts and a second parts are s	grang end	æ.	om:		
po ná	e e e e e e e e e e e e e e e e e e e	ж.			
Fig. CTP 64			ا خو		
roups that react with and thereby bind the zeolite.	lite bound in	n a po	ZEOLITE BOUND IN A POLYMER MATRIX  olymer matrix, with the matrix comprising a polymer having function ing material can be extruded into thin films or fibers, thereby making. The odor absorbing material can also be used in other application.		
equiling absorption of odor causing compounds.	•	zn (	*		
O gar or			*		
405 44					
·-					

# FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

					Spare"		•
AL	Albania	ES	Spain	LS 🖘	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal .
AU	Australia	GA	Gabon	· LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	ТJ	Tajikistan
BE	Belgium .	GN	Guinea	, MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	иU	Hungary	ML,	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN.	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	υG	Uganda 🐡
BY	Belarus	IS	Iceland ~	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX .	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan .	NE	Niger	VN *	Viet Nam
CG	Congo	KE	Kenya	'NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO 🖵	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		,
CN	China	KR	Republic of Korea	PТ	Portugal .	•	
CU	Cuba	KZ	Kazakstan	RO	Romania		•
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		*
DE	Germany	Li	Liechtenstein	SD	Sudan		- > 49,
DK	Denmark	LK	Sri Lanka	SE	Sweden		•
EE	Estonia	LR	Liberia	SG	Singapore	e y Sand"	
				.+			

# ODOR ABSORBING MATERIAL COMPRISED OF A ZEOLITE BOUND IN A POLYMER MATRIX

## FIELD OF THE INVENTION

5

10

15

20

25

The present invention relates to odor absorbent materials comprised of a zeolite bound in a polymer matrix. The present invention also relates to odor absorbent articles employing such odor absorbent material. In particular, such odor absorbent articles include diapers, sanitary napkins, and tampons, as well as any other articles useful in applications where the absorbance of odor causing compounds, especially amines, is required.

# BÄCKGROUND OF THE INVENTION

Absorbent pads designed to be worn by humans to absorb bodily fluids, such as urine, menstrual fluid, perspiration, etc., include such articles as disposable diapers, sanitary napkins, panty shields, underarm shields, and incontinence pads. In use, these articles release malodorous vapors due to human bodily fluid. The most common type of compound which creates malodorous vapors in humans is amide compounds.

Particular problems are often associated with tampons. Tampons can have a strong odor since the menstrual fluid contains amines, and in particular trimethylamine which releases malodorous vapors. An article which can absorb the bodily discharge as well as the odor-causing amines contained in such a discharge may be of great value and may be commercially attractive. There is still a need for an absorbent article that, while exhibiting good liquid transfer properties and absorbing properties for bodily fluids, can also exhibit excellent odor adsorption.

Accordingly, it is an object of the present invention to provide an odor absorbing material which can effectively remove odor causing compounds from a fluid, liquid or gas.

2 -

Yet another object of the present invention is to provide an odor absorbing material which can effectively absorb odor causing amines compounds.

Another object of the present invention is to provide an odor absorbing material which can effectively absorb odor causing amine compounds generated from the decompositions of the biological waste.

Still another object of the present invention is to provide an article containing the odor absorbing material of the present invention which is useful in absorbing the odor causing amine compounds contained in a bodily discharge.

A further object of the present invention is to provide an article having a zeolite contained in a polymer matrix that, in the presence of an aqueous solutions, the polymer matrix acts a barrier to the water and thus, prevents the odor causing amine compounds from being displaced by water in the zeolite.

Another object of the present invention is to provide such an odor absorbing material which can also be useful in application such as shoe liners, masks and air filters.

These and other objects of the present invention will become apparent upon a review of the following - specification and the claims appended thereto.

## SUMMARY OF THE INVENTION

5

10

15

20

25

30

35

In accordance with the foregoing objectives, there is provided an absorbing material comprised of a zeolite bound in a polymer matrix... An example of a class of zeolites which can be used in this present invention are odor absorbing zeolites. The polymer matrix helps—contain the fine particles of the zeolite while also aiding in the handling and incorporation of the odor absorbing material into an odor absorbing article, such as

10

20.

25

ے 30

35

- 3 -

a pad or tampon.

The odor absorbing material of the present invention is useful in absorbing odor-causing compounds such as amines. Particular applicability is thereby found in absorbent articles such as tampons, feminine pads, diapers, sanitary napkins, panty liners, incontinent garments, as well as any other type of article which can be placed in an appropriate location to absorb amine based odors. The odor absorbing material of the present invention provides one with an efficient and effective means of absorbing amine-based, as well as other types of odors.

# DETAILED DESCRIPTION OF THE INVENTION

The odor absorbing materials of the present invention contain a zeolite. In one embodiments, the zeolite is a potassium or sodium aluminum. Natural zeolites that can also be used in the present invention including analcite, chabazite, heulandite, natrolite, stilbite, and thomsonite.

A preferred class of zeolites for use in the present invention are molecular sieves. In one embodiment, the molecular sieves are selected from the group of crystalline aluminosilicate materials.

Typically, the crystalline structures of the molecular sieves are interlaced with regularly spaced channels and molecular dimensions forming a network of uniform pores.

The network of uniform pores may comprise almost 50% of the total volume of crystals. Other types of molecular sieves that may be used in the present invention are listed in the Handbook of Molecular Sieves compiled by Rosemarie Szostak, VanNordstrom Reinhold, 1984, which is

Generally, the zeolite chosen for use in accordance with the present invention should have a

hereby incorporated by reference.

5

10

15

20

25

30

sufficient pore size to absorb the amine compound. And, for other odor compounds, the molecular sieve should have sufficient pore size to absorb the pertinent\_odor compound. It has been found that, in dealing with amine odor compounds, the zeolite employed should contain acidic groups. In another embodiment, zeolites, which are commercially available, which contain silanol groups and which are very weak acids, react with amine compounds and thus, are effective in removing the amine compounds as an odor problem.

Another class of zeolites that can also be used in the present invention is characterized as "intermediate" silicate/aluminate zeolites. The intermediate zeolites are characterized by SiO2/AlO2 molar ratios of less than about 10. The intermediate zeolites have a high affinity for amine-type odors, they are weight efficient for odor absorption because they have a larger surface area, and they are moisture tolerant. A wide variety of intermediate zeolites suitable for use herein are commercially available as Valfor Registered TM CP301-68, Valfor Registered TM 300-63, Valfor Registered TM CP300-35, and Valfor Registered TM 300-56, available from PQ Corporation, and the BCV100 Registered TM series of zeolites from Conteka.

A further type of zeolites that may be used in the present invention include modified zeolites treated with an organic group in order to enhance the characteristics of the zeolite. Examples of such zeolite materials are marketed under the trade name Abscents Registered TM and Smellrite Registered TM, available from UOP. These materials are typically available as a white powder in the 3-5 micron particle size range. Such materials may also be used for control of sulfurcontaining odors, e.g., thiols, mercaptans.

In another example, by changing the

characteristics of the zeolite, the range of use with different polymer matrices of the present invention may be increased. For example, a more hydrophobic zeolite may be more easily added in mixture with polyethylene, polypropylene or polystyrene.

For the present invention, the zeolite is bound in a polymer matrix. By chemically binding the zeolite to the polymer so as to form a polymer matrix, the zeolite is in a safe form (e.g. contained in the matrix and thus, not a powder) that may then be used on or near the skin.

In one embodiment, the polymer of the present invention is modified to contain a carboxylic acid or anhydride functional groups to react with and hence bind the zeolite to the polymer. It is through this reaction and binding effect that the zeolite is able to remain stably within the matrix. In addition, the carboxylic acid groups or anhydride groups in the polymer matrix aids in the attraction and migration effect and its adsorption of the odor causing compounds. Other polymers containing acid groups such as sulfunates, sulfates, phosphates, acrylates, phorphones or other groups which in solution can react with amines to form a salt, such as anhydride polymers, may also be used in the present invention.

In another embodiment of the present invention, the polymer matrix is comprised of a film-forming polymer. Such film-forming polymers can comprise any suitable film-forming polymer which permits the migration of a compound such as an amine. The film forming nature of the polymeraids in the extrusion of the odor absorbing material as a film or as fibers. For the present invention, film forming polymers include the polyacrylate, polyethylene acrylic acid, polyethylene maleic anhydride, or polystyrene maleic anhydride polymers.

The mechanism believed to be involved in the odor absorption relates to the amine initially being

10

20

5

10

15 ...

20

25

30

35

absorbed and reacting with the acidic groups of the polymer matrix. As equilibrium is established, the amine compound moves to the zeolite where it is adsorbed. As a result, the amine keeps moving to the polymer matrix and then on to the zeolite adsorbent. In one embodiment, polymers containing ethylene are used as they are more porous to the amines and permit ready migration of the amines into the matrix and hence onto the zeolite adsorbent contained in the matrix.

The polymer and zeolite may be blended and reacted in any conventional manner. One example of forming the odor absorbing material of the present invention is by blending the polymer and the zeolite in a commercial mixer, such as a Henschel mixer. The zeolite is often available in a dried and finely ground particulate form. Polymers are often available in pellet or particulate form. In one embodiment of the present invention, the blend is then fed through a conventional extruder to react the zeolite with the polymer and to form a film which is formed by the film-forming polymer. Alternatively, in another embodiment, the materials can be fed directly to the extruder and thus, both blended and reacted in the extruder.

If desired, other forms of the odor absorbing material of the present invention can be made for the intended end use. The film, for example, can be made in thin strips, or the odor absorbing material can be extruded in the form of fibers. The material can also be extruded as granules, pellets, or can be extruded to coat a screen mesh which can subsequently be used in a urinal; a mask or an air filter.

In another embodiment of the present invention, plasticizers or additional resins can also be added to the blend of the present invention in order to modify the characteristics of the final product. For example, to

- 7 -

improve the pliability and softness of the material, a styrene-butadine elastomer and an oil can be added to the blend of zeolite and polymer prior to or during extrusion. Other suitable modifiers can also be added for a desired purpose.

The odor absorbing material of the present invention can be used in many different articles. Generally, the application of the material will involve absorption of fluid discharges containing malodorous chemical compounds including acyclic and cyclic amines, aldehydes, fatty acids, and sulfur-containing compounds such as sulfides. Vaginal secretions and used menstrual pads may contain malodorous chemical compounds; for example, trimethylamine, pyridine, furaldehyde, isovaleric acid and methyl mercaptan. For example, applications of the odor absorbing material of the present invention include pads, diapers and sanitary napkins.

15

30

As an illustration of the use of the present inventions, a tampon employing the odor absorbing material of the present invention can comprise a multilayer structure. The odor absorbing material of the present invention would be in the form of a film which is placed in between two absorbent layers. This multilayer structure is then formed into a tampon. During use, the absorbent layers would absorb the menstrual fluid, while the matrix film layer in between the absorbent layers would absorb the odor causing amine compounds, generally trimethylamine, and hence remove the odor.

In another example, the odor absorbing material of the present invention could similarly be used in a feminine pad, diaper or panty liner. For example, this liner, diaper or pad would also be comprised of a multilayer structure. The top layer would be absorbent, fluid-permeable fabric. An absorbent pad behind the non-woven fabric would serve as a fluid absorbing holder.

5

10

15

20

25

30

35

Such pads, for example, can comprise an elastic sheet full of cavities or pores and can comprise an accumulation of ground wood pulp or other absorbent material such as material comprised of the sodium or potassium salt of polyacrylic acid. The material of the present invention can be situated within the pad or on either side or both sides of the pad to effectively eliminate the amine odorcausing contained in any bodily discharge. The final layer of the diaper would be a backside surface layer which is fluid impermeable and generally is a polyethylene film.

While use with regard to bodily discharges is one application of the odor absorbing material of the present invention, the odor absorbing material can also be used in other applications. For example, an odor absorber in accordance with the present invention for amine-based odors can be applied conveniently in fish wrapping or in a covering for animal waste. In such an example, a film comprised of the odor absorbing material of the present invention would be suitable for such applications of the present invention. In another example, bags containing fish or animal waste can be lined with the odor absorbing material of the present invention. The material of the present invention can also be made into strips that can be used in garbage bags. Such strips can also be used in hospital dishes used for urine collection, or in portable toilets in which the bodily discharge is contained in a compartment. The strips can be contained within such a compartment. The odor absorbing material of the present invention can also be used to coat urine screens as used in public urinals. The material of the present invention can also be used in masks for working conditions involving odorous environments, or in air filters or in air fresheners. The odor absorbing material can also be used as a film in a shoe odor absorbing article. - The odor absorbing material can also be part of an article which

- 9 -

has a velcro tab for attachment to clothing, bandages, gloves or the like. In any suitable application, the matrix polymer of the present invention can be modified or is chosen for characteristics to better effect the application.

The present invention will be illustrated in greater detail by the following specific examples. It is understood that these examples are given by way of illustration and are not meant to limit the disclosure or the claims to follow. All percentages in the examples, and elsewhere in the specification, are by weight unless otherwise specified.

### EXAMPLE 1

An odor absorbing material in accordance with the present invention is made by mixing together 40 wt. % of polyethylene acrylic acid 2,200 available from du Pont Chemical Company and 60 wt. % of Abscent 2000 modified zeolite available from UOP. The blend was mixed in a Henschel blender and compounded at 350°F in a single screw extruder. A film was extruded.

The film was tested for its capacity to absorb trimethylamine. The method employed was to add 1 ml of trimethylamine [0.1N] to 100 ml of distilled water. A large 2x4 inch piece of the film was then added to the solution. After 4 hours, three drops of Methyl Orange indicator was added and the solution containing the film was titrated with sulfuric acid [0.1N] until a color change was achieved so as to determine how much of the amine was consumed by the film. The results demonstrated that the material was effective in absorbing all of the amine in solution.

25

10

- 10 -

## EXAMPLE 2

Another odor absorbent material in accordance with the present invention was prepared by mixing together 40 wt. of a polyethylene maleic anhydride available from Union Carbide under the designation DEFA 1373, and 60 wt. % of Absent 2000 modified zeolite available from UOP. The blend was mixed in a Henschel blender and then compounded at 350°F through a single screw extruder to form a film. A 1 gram piece of the film was then tested for its availability to absorb trimethylamine in accordance with the procedures described in Example 1. The results demonstrated that the odor absorbance material was effective in removing the odor causing trimethylamine from the solution.

15

35

10

5

### EXAMPLE 3

An odor absorbing material in accordance with the present invention was prepared by blending together 50 wt. % of Abscent 2000 modified zeolite available from UOP, 25 wt. % of a polyethylene maleic anhydride available from 20 Union Carbide under the designation DEFA 1373, 10 wt. % of a styrene butadiene rubber and 15 wt. % of a mineral oil. The blend was compounded at 350°F through a single screw extruder. The resulting product was then placed into a platen and pressed at 350°F into a 10 to 15 mil film. The 25 film was then tested for its ability to absorb trimethylamine in accordance with the procedure described in Example 1. The results demonstrated that the film worked very well in adsorbing trimethylamine. As well, it demonstrated very soft and very flexible characteristics. **30** -Due to the presence of a styrene butadiene rubber-and mineral oil, the film was softer and more flexible than~ either of the films prepared in Examples 1 or 2.

While the invention has been described with preferred embodiments, it is to be understood that

- 11 -

variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.

5

10

15

20

#### What is claimed is:

- 1. An odor absorbing material comprised of a zeolite bound in a polymer matrix wherein the matrix comprises a polymer with functional groups.
- 2. The odor absorbing material of claim 1, wherein: (a) the polymer is selected from the group consisting of polyacrylate, polyethylene acrylic acid, polyethylene maleic anhydride and polystyrene maleic anhydride; and (b) the zeolite is selected from the group of modified zeolites and intermediate silicate/aluminate silicates.
- 3. The odor absorbing material of claim 1, wherein the zeolite contains silanol groups.
  - 4. The odor absorbing material of claim 1, wherein the zeolite is comprised of a molecular sieve.
- 5. The odor absorbing material of claim 1, wherein the material is in the shape of a film.
- 6. The odor absorbing material of claim 1, wherein the polymer is comprised of a polyethylene acrylic acid.
  - 7. The odor absorbing material of claim 1, wherein the polymer is comprised of a polyethylene maleic anhydride.
  - 8. The odor absorbing material of claim 1, wherein the polymer is comprised of polystyrene maleic anhydride.

5

15

- 9. The odor absorbing material of claim 1, wherein the polymer is comprised of a polymer containing carboxylic acid or anhydride functional groups that binds the zeolite to the polymer.
- amines contained in a bodily discharge comprising the odor absorbing material of claim 1.
- 11. The article of claim 10, wherein the article is a tampon.
  - absorbing material is in the form of a film or fabrics; placed in between two water absorbent layers.
  - \_\_\_\_ 13. The article of claim 10, wherein the \_article is a diaper.
- 20 14. The article of claim 10, wherein the article is a sanitary napkin.
  - 15. The article of claim 10, wherein the article is a pad.
  - and the odor released from such discharge, comprising the steps of:
  - (a) providing an article comprising a zeolite bound in a polymer matrix;
    - (b) exposing the article to the bodily
      discharge;
      - (c) absorbing the odor.

- 14 -

17. The method of claim 16, wherein the article is a tampon.

- 18. The method of claim 16, wherein the article is a diaper.
  - 19. The method of claim 16, wherein the article is a sanitary napkin.
- 10 20. The method of claim 16, wherein the article is a pad.
- 21. An article for absorbing odor which contains the odor absorbing material of claim 1, with the odor absorbing material being in the shape of a film or fibers.
  - 22. The article of claim 21, wherein the article is in the shape of a shoe liner.  $\sim$   $\sim$
- 23. The article of claim 21, wherein the article is in the shape of a strip which can be placed in garbage bags, waste coverings or urine containing compartments.
- 24. The article of claim 21, wherein the article is in the form of a mask.
- 25. The article of claim 21, wherein the

  article is in the form of a pad with a velcro tab for attachment to a piece of clothing or gloves.

- 26. A method of forming an odor absorbing material comprising the following steps:
  - (a) blending a polymer and zeolite;

..-.15 -

(c) forming a shaped article comprising the zeolite bound in a polymer matrix:

10

15

20,

25

#### INTERNATIONAL SEARCH REPORT

Form PCT/ISA/210 (second sheet)(July 1992) \*

International application No. PCT/US99/02760

	THE STATE OF SUPERCY MATTER						
A. CLASSIFICATION OF SUBJECT MATTER							
IPC(6) :A61F 13/15; A61M 01/00							
US CL: 604/317, 359 According to International Patent Classification (IPC) or to both national classification and IPC							
A 3							
B. FIELDS SEARCHED							
Minimum d	ocumentation searched (classification system followed	by classification symbols;	er Fel arrin				
U.S. : 424/76.1, 76.5, 76.6; 604/317, 359, 360, 368							
Designates	ion searched other than minimum documentation to the	extent that such documents are included	in the fields searched				
Documentat	foli scricing onto, and timening commenced to an						
	- Aug.	**					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)							
Electronic o	THE DARK COURTINES GOLING THE THEFTHERIONER SCHICK (1977)	ine of the base and, where practices.	× ×				
			<b>∴</b> ⊎				
			±200 <b>6</b> 00 450				
	UMENTS CONSIDERED TO BE RELEVANT	. 😜	-, b				
C. DOC							
Category*	Citation of document, with indication, where app	propriate, of the relevant passages	Relevant to claim No.				
.,	TIC E ADDEDO A CEDINIL et al. DA Tulu	1005 col >95 lines 32-51	1, 2, 9-11, 13-20,				
<b>X</b> <sub>r/r</sub>	US 5,429628 A (TRINH et al) 04 July	1995, Col. 25 mics 52-51.	26				
		***	20				
Y	4	The state of the s	4 0 12 21 25				
			4-8, 12, 21-25				
		1001	4 5 01 05				
Y	US 5,037,412 A (TANZER et al) 06 A	August 1991, col. 5 lines 42-	4, 5, 21-25				
	59, col. 8 line 48 to col. 9 line 23.		-				
	ii.	<b>&amp;</b>					
			ž.				
	χ.	, «æ	4.1 4.00				
	·						
	No.	- CT					
		*					
	•		*				
	·	•	*				
			<del>-</del>				
Furt	her documents are listed in the continuation of Box C	. See patent family annex.	Sec.				
• S <sub>7</sub>	ocial estegories of cited documents:	"T" later document published after the int					
	cument defining the general state of the art which is not considered	date and not in conflict with the app the principle or theory underlying th					
	be of particular relevance	"X" document of particular relevance; th					
	rlier document published on or after the international filing date seument which may throw doubts on priority claim(s) or which is	considered novel or cannot be considered novel or cannot be considered when the document is taken alone	ered to involve an inventive step				
ci	ted to establish the publication date of another citation or other	"Y" document of particular relevance; the	se claimed invention cannot be				
	ecial reason (as specified)	considered to involve an inventive	step when the document is				
	seument referring to an oral disclosure, use, exhibition or other `` eans	combined with one or more other such being obvious to a person skilled in					
	ocument published prior to the international filing date but later than the priority date claimed	"&" document member of the same pater	nt family				
Date of the actual completion of the international search  Date of mailing of the international search report							
25 APRIL 1999							
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks  Authorized officer							
Box PCT Washington, D.C. 20231  MARK O. POLUTTA							
Facsimile No. (703) 305-3230 Telephone No. (703) 308-2114							